

XIV. THE COLLODION PROCESS.

In the Seventh Edition of PHOTOGENIC MANIPULATION, published in January 1851, Collodion was mentioned, amongst many other things, as having been used by the author to form an adherent film on glass-plates on which to apply the sensitive coating of iodide of silver; he, in conjunction with Mr. Cundell, having tried many experiments with it: but as they developed their pictures with the simple gallic acid, instead of the pyro-gallic, as subsequently used by Mr. Archer, they did not discover the great sensitiveness which has since made the Collodion such a favourite process for portraiture.

Pyro-gallic acid was first obtained by Scheele by sublimation from galls; and was considered as identical with gallic acid. It may be obtained by heating gallic acid, previously dried, in a small retort placed in an oil-bath to a temperature of 410° to 420° . It, however, requires considerable care in the preparation; and we refer our readers to Dr. Stenhouse's valuable papers on this substance, published in the Memoirs of the Chemical Society in 1842. We are unable to state who first applied pyro-gallic acid to photography.

The preparation, properly called iodized Collodion, may now be obtained of the publishers, ready for use, and will save the inexperienced operator much time, if not loss, in preparing it himself; but for the sake of those who would prefer making their own, or who, residing abroad, have it not in their power to purchase, we give the method of preparation.

Collodion being itself obtained from gun-cotton, it will be necessary first to describe the method of preparing this peculiar and extraordinary substance, discovered, and subsequently patented by Professor Schonbein.

Take some perfectly clean-carded cotton, such

as is used for polishing Daguerreotype plates, and thoroughly immerse it in a mixture previously made of equal parts, by weight, of nitric acid, s.g. 1.45, and sulphuric acid, s.g. 1.845; allow it to remain about three or four minutes, and then remove it into a large vessel of clean water, and well wash it so as to free it from all traces of acid; it is then to be taken out and washed in distilled water; after which it must be dried by means of bibulous paper and a very gentle heat, not exceeding 212° . To one ounce of this gun-cotton add seven ounces of sulphuric ether; when the solution is complete, and the ether appears saturated, the clear portion should be carefully strained off. This is Collodion, a very mucilaginous solution, and as, in this state, it would be found too thick to flow easily on the glass-plates, it must be diluted with about its equal bulk of ether.

The operator must now dissolve 160 grains of crystallized nitrate silver in four ounces of water, and 166 grains of iodide potassium in two ounces of water. On the addition of the iodide potassium to the silver solution, a precipitate of iodide of silver is formed; this must be well washed in distilled water. The precipitate of iodide of silver is then to be dissolved in a saturated solution of iodide of potassium, the precipitate being added also to saturation. This solution, containing the double salt of iodide of silver and iodide of potassium, is next to be added to the Collodion, till a turbidness is visible, which is the indication of sufficient having been added. The iodized Collodion is now completed, and only requires to be left till it is clear and bright, when it should be of a light straw colour; if darker, it is an indication of the presence of acid either in the ether or gun-cotton.

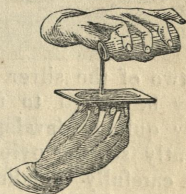
Preparation of the Glass-Plates.—The operator must now take a glass-plate, the size of which fits his camera frame, and it will be found very convenient to adopt the sizes of the Daguerreotype plates, and

thoroughly clean it by carefully removing from its surface all grease; the method by which this is effected is not material, some use a little tripoli, others simple washing, while many prefer to use a little ammonia. The clean plate is now to be supported on the fingers

FIG. 1.



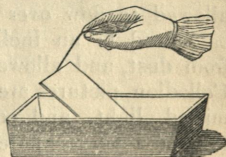
FIG. 2.



of the left hand, as in Figure 1, or it may be held by a piece of India rubber, the surface of which has been made adhesive by melting it, as in Figure 2; and a sufficient quantity of the iodized Collodion poured upon the centre of it as will well cover it; by the motion of the hand the Collodion is made to run over the whole surface of the plate; one of the corners is then inclined downward, and the whole of the superfluous Collodion poured back into the bottle, by drawing the mouth of which along the edge of the glass-plate, the lines first formed will run one into the other, and give a flat even surface. A little

practice will soon enable the operator to accomplish this process with facility, though it may appear somewhat difficult by the description. The plate being now coated with the iodized Collodion, should be immediately placed in a bath of nitrate of silver. Figure 3 represents the method of immersing it;

FIG 3.



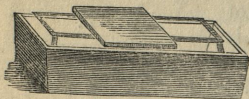
thirty grains of nitrate of silver are dissolved in one ounce of water, and this being placed in the square vessel, and the plate held up by a bent wire-holder, is raised and lowered three or four times till the silver solution flows equally over the

surface; it is now, in its wet state, and before the ether has had time to evaporate, placed in the dark frame of the camera, and should be used immediately, as much depends upon it; if used at once, it is as sensitive as a Daguerreotype plate, some consider it to be more so. On removing the plate from the camera, no image is visible; the following is the method of developing it. A solution is made consisting of

Pyro-gallic acid	3 grains,
Glacial acetic acid	1 dram,
Distilled water	1 ounce,

and the plate being supported on a levelling-stand

FIG. 4.



placed in a glass or porcelain dish (Fig. 4), the developing mixture is flooded over it, and made to flow all over the plate.

In very dull weather, a drop or two of the silver solution, 30 grains to the ounce, may be added to the mixture. The impression is very quickly developed; and as soon as it is sufficiently so, the pyro-gallic mixture must be removed by carefully flooding the plate with water. After which, it is to be treated with a saturated solution of hypo-sulphite of soda; this immediately removes the iodide of silver, leaving those portions of the picture which are to form the dark parts of the positive, beautifully transparent. The plate is to be again flooded with simple water, to remove all the hypo-sulphite; a stream of distilled water being then allowed to flow over it, it is now finished, and must be placed in an inclined position, carefully guarded from dust, and allowed to dry spontaneously. These Collodion pictures are more or less negative by transmitted light, and positive by reflected: the addition of a very minute quantity of nitric acid tending to increase the latter effect. As the Collodion film is very tender, great care should be taken of the plates.

We shall now proceed to describe some of the modifications of the above process which have from time to time been suggested by various operators. In place of pyro-gallic acid, both the proto-nitrate and sulphate of iron have been used as the developing agent.

In the December number of the "Practical Mechanic's Journal" appeared the following modification of the Collodion process; and as it appears to possess some advantages, we give our readers the benefit of it. The writer states that it is unnecessary to add iodide of silver to the Collodion, as the addition of iodide of potassium alone, on immersion in the nitrate of silver, forms the required coating of iodide silver upon the glass.

In the preparation of the gun-cotton, in the place of the nitric acid, nitre is recommended. "Equal bulks of sulphuric acid and nitre will be found to answer best. The cotton being immersed in this mixture, and well saturated with it for about seven or eight minutes, is then taken out and thoroughly washed in water, and dried. The iodizing process is simply effected thus:—To *pure* sulphuric ether add about one-eighth of its bulk of alcohol, then a little iodide of potassium, and after this the prepared cotton: let these be well shaken together for some time, and then allowed to settle. Four or five grains of iodide to the ounce of ether will be found sufficient.

"The admixture of alcohol to the ether seems to be necessary in preparing Collodion for our present purpose, as it will be found, if pure ether be employed, that little or no coating will be formed on immersion in the nitrate of silver. It must at the same time be observed, on the other hand, that when too much alcohol is added, the coating will be too opaque, preventing the light from penetrating. Thus, little more than the surface of the sensitive coating being acted upon, it is impossible to obtain a bold picture. It is difficult, by description, to point out the depth

of coating required; but a very little experience will be sufficient to determine this. The object is to avoid the extremes above-mentioned, viz., the having little or no coating at all, and the having one too opaque.

“From the difficulty I have experienced in always obtaining pure ether (there being often a considerable quantity of alcohol already mixed with it), I have been obliged to adopt the following mode of preparing iodized Collodion:—To 1 oz. of ether add 5 or 6 grs. of iodide of potassium, and shake them well together for some time; after settling, the iodized ether should be poured off, and some of the prepared cotton added to it, till the proper consistency is attained. Now prepare a solution of iodide of potassium in alcohol, and add this to the iodized Collodion till the coating formed by immersion in the silver solution is considered sufficiently deep. This should be of a milk-like appearance, but, at the same time, considerably transparent, for reasons before given. By this means I am enabled, with ease, to modify my Collodion so as to obtain any depth of coating I may desire; the only objection attending this adulteration being, the having to pay the price of ether for so much alcohol, which every one knows is considerably cheaper. My next modification is in the preparation of the developing mixture. It will be noticed that pyro-gallic acid is recommended for this purpose, the acetic acid being added to prevent the pyro-gallic from attacking the parts unaffected by light. This, in common with most other acids, it effects; but I have never been able by its use to obtain a pure white; from this circumstance I was led to try the effects of other acids, and found nitric to answer my purpose. A difficulty, however, arose in the nice adjustment required in the proportions of the two acids, which induced me to try another well-known developing agent—sulphate of iron; and the result obtained in this way was quite satisfactory.

The proportions in this case seem to be of much less importance, so that, with very little care, an excellent developing mixture may be obtained. I subjoin the proportions which I have used with success :—

Sulphate of iron	12 grains,
Nitric acid	1 or 2 drops,
Water	1 ounce.

If, from any variation in the strength of the nitric acid, the dark parts of the picture should be spoiled by the action of the sulphate, the addition of a little more acid will be found to prevent the evil."

As we have before stated, the Collodion plate rapidly loses its sensitiveness on becoming dry ; to remedy this, and enable the operator to keep it ready prepared for an indefinite period, Mr. Archer recommends a plan which he has found to answer perfectly : this is to take the impression while the plate is in a bath of nitrate of silver ; the bath is made of two pieces of plate glass, connected together at the sides and bottom, and gradually tapering downwards, so as to form a narrow wedge-shaped vessel, the top being about three-eighths of an inch, and the bottom one-eighth. This bath is made to fit tightly into a dark sliding frame fitting the camera. The bath is about three parts filled with a solution of nitrate of silver of the usual strength ; the prepared plate is plunged into it, and the light acts on the prepared film whilst in the bath.

We are indebted to Mr. Fry for a method by which the hitherto tender Collodion film is rendered tougher ; indeed, so much so that, if necessary, after its final washing, it may be dried by bibulous paper, which gives it this advantage—that the picture may be finished immediately.

These Collodion pictures are all either positives or negatives, according as they are viewed by reflected or transmitted light. Mr. Archer gives the following

process for increasing at pleasure these effects, or, as he terms it, whitening or blackening them. It is similar to Mr. Hunt's process, as applied to paper negatives. The negative, after being fixed with the hypo-sulphite of soda, is thoroughly well washed in water. To a saturated solution of bichloride of mercury in hydro-chloric acid, add six parts of water: a sufficient quantity of this solution is flooded evenly over the glass plate; this will be found to deepen the tones of the picture considerably, and the positive image will almost entirely disappear; but presently a peculiar whitening effect will come on, and in a short time a delicate white picture will be developed, the negative character of the image being almost destroyed. This picture can be washed, dried, and preserved, as a positive photograph. But if, after the washing, it is placed in a weak solution of hyposulphite soda, in a short time the white picture will disappear, and a deep-toned negative, some shades darker than the original, will be the result.